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PATENT

*Hubertus  
Spaepen  
C-887*

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Hubertus A. Spaepen

Art Unit:

1754

Serial No.:

09/248,392

Attorney Docket No.: GB97/023

Filed:

February 12, 1999

Entitled:

"PRODUCTION OF PRODUCTS  
CONTAINING PRECIPITATED  
CALCIUM CARBONATE"

TRANSMITTAL OF CERTIFIED COPY

ECC International Inc.  
Calgon Center  
P. O. Box 1346  
Pittsburgh, PA 15230  
April 30, 1999

Assistant Commissioner For Patents  
Washington, D.C. 20231

Sir:

Enclosed is the certified copy of the foreign application from which priority is claimed for this case:

Country:

United Kingdom

Application Number:

9802999.4

Filing Date:

February 13, 1998

Respectfully submitted,

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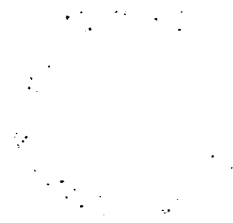
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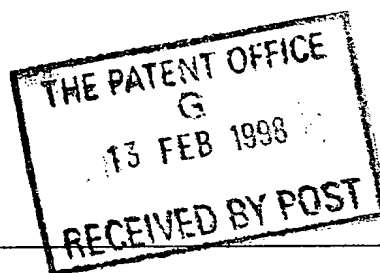
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Dated 12 February 1999



The  
Patent  
9802999.4

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01/7700 25.00 9802999.4



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1. Your reference

GB97/023

2. Patent application number

(The Patent Office will fill in this part)

9802999.4

3. Full name, address and postcode of the or of each applicant (underline all surnames)

ECC INTERNATIONAL LTD  
1015 ARLINGTON BUSINESS PARK  
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READING, BERKSHIRE  
RG7 4SA  
UNITED KINGDOM

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

00 44005 7004

4. Title of the invention

PRODUCTION OF PRODUCTS CONTAINING PRECIPITATED  
CALCIUM CARBONATE

5. Name of your agent (if you have one)

MCCORMACK, DEREK JAMES

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

ECC INTERNATIONAL LTD  
PATENTS DEPARTMENT  
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Patents ADP number (if you know it)

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6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
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# Patents Form 1/77

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Description

30

Claim(s)

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Abstract

1

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Priority documents

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Statement of inventorship and right to grant of a patent (Patents Form 7/77)

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Request for preliminary examination and search (Patents Form 9/77)

1

Request for substantive examination (Patents Form 10/77)

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Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

Derek McCormack

Date

12 FEBRUARY 1998

12. Name and daytime telephone number of person to contact in the United Kingdom

DEREK MCCORMACK TEL (01726) 818223

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PRODUCTION OF PRODUCTS CONTAINING PRECIPITATED  
CALCIUM CARBONATE

The present invention relates to the production  
5 of products containing precipitated calcium  
carbonate. In particular, the present invention  
relates to a method of producing precipitated calcium  
carbonate in an aqueous medium optionally containing  
non-consumable solids to be entrained by and bonded  
10 to the calcium carbonate.

Synthetic production of calcium carbonate for  
~~use as a fine particulate pigment material in~~  
applications such as paper filling and paper coating  
is well known.

15 It is also known from EP-A-0604095 that a fine  
particulate solid, eg waste material may be rendered  
more easily separable from an aqueous medium in which  
it is suspended if an alkaline earth metal carbonate,  
and particularly calcium carbonate, is precipitated  
20 in the aqueous suspension in such a way that the fine  
solid material becomes entrained in and bonded to the  
crystals of the alkaline earth metal carbonate  
precipitate.

Other prior art references describe the  
25 production of precipitated calcium carbonate in an  
aqueous medium containing other non-consumable  
solids, eg fibres of the kind used in paper making,

the composite product then being useful in paper making.

Methods of producing precipitated calcium carbonate, whether or not containing entrained and/or  
5 bonded non-consumable solids, are well known.

TAPPI Monograph Series No. 30, "Paper Coating Pigments", pages 34-35 describes three main commercial processes for preparing precipitated calcium carbonate which is especially suitable for  
10 use in preparing products for use in the paper industry. In all three processes limestone is first calcined to produce quicklime, and the quicklime is  
then slaked in water to yield calcium hydroxide or milk of lime. In the first process the milk of lime  
15 is directly carbonated with carbon dioxide gas. This process has the advantage that no by-product is formed, and it is relatively easy to control the properties and purity of the calcium carbonate product. In the second process the milk of lime is  
20 contacted with soda ash to produce by double decomposition a precipitate of calcium carbonate and a solution of sodium hydroxide. The sodium hydroxide must be substantially completely separated from the calcium carbonate if this process is to be  
25 commercially attractive. In the third main commercial process the milk of lime is first contacted with ammonium chloride to give a calcium chloride solution and ammonia gas. The calcium



chloride solution is then contacted with soda ash to produce by double decomposition precipitated calcium carbonate and a solution of sodium chloride.

If the calcium carbonate-containing product is  
5 to be used as a filler or as a coating pigment in the paper industry, it is generally preferred to use the first process described above, namely the direct carbonation of milk of lime with carbon dioxide-containing gas, because this process yields no  
10 undesirable by-products which have to be removed before the calcium carbonate-containing product can be used in the paper industry. Generally the process of carbonating milk of lime is carried out on a batch basis. A vessel is charged with a quantity of milk  
15 of lime at an appropriate temperature and concentration, and carbon dioxide-containing gas is admitted into the vessel, generally in the form of fine bubbles. Mechanical stirring means may be provided to ensure good mixing of the contents of the  
20 vessel, and to promote the formation and continuation of small bubbles of the carbon dioxide-containing gas. The admission of the carbon dioxide-containing gas is generally continued until substantially all of the calcium hydroxide present has been converted into  
25 calcium carbonate. This may conveniently be indicated by monitoring the pH of the suspension in the vessel. When the pH has fallen to around 7, at which level the suspension has a substantially

neutral reaction, the reaction is deemed to be complete. The process may be conducted in two or more stages with vessels of the type described above connected in cascade, but each stage still takes  
5 place on a batch basis. The batch process generally has the disadvantage of requiring a high degree of supervision, and variations in the product tend to occur from batch to batch. It would be desirable to be able to operate the calcium carbonate  
10 precipitation process on a completely continuous, rather than a batch, basis. The reactants move progressively through the reaction zone in a  
continuous reaction. It is necessary to provide a process plant which will allow the reactants adequate  
15 residence time in the plant for substantially complete carbonation of the calcium hydroxide to occur. The residence time which the reactants spend in the plant is proportional to the length of the path followed by the reactants through the plant.  
20 Thus in order to increase the residence time, it is necessary to increase the physical size of the plant, which in turn increases the capital cost of the plant. It is therefore important, from an economic point of view, that the chemical reaction of the  
25 carbonation of the calcium hydroxide should take place as rapidly as possible.

WO-A-97/05061 (Unikristal) describes a plant for continuous production of precipitated calcium

carbonate. The plant generally comprises from 10 to 15 interconnected cells, each of which is provided with an inlet conduit for a suspension comprising calcium hydroxide, an outlet conduit for a suspension  
5 of partially carbonated calcium hydroxide, a propeller-type stirrer rotated by means of a hollow shaft, down which carbon dioxide-containing flue gas is supplied, the shaft being surrounded by a cylindrical tube. The inlet conduit communicates  
10 with the space between the shaft and the cylindrical tube, and the outlet conduit passes through the outer wall only of the cell, and draws suspension from the  
part of the cell between the cylindrical tube and the cell wall. When the stirrer is set in motion, the  
15 level of suspension near the cell wall rises, causing suspension to overflow through the outlet conduit, and at the same time drawing fresh suspension in through the inlet conduit. Meanwhile, carbon dioxide-containing gas is passed down through the  
20 shaft and is dispersed by the stirrer to rise through the suspension in the form of fine bubbles, which are said to provide a large area of contact between the calcium hydroxide-containing suspension and the carbon dioxide gas. Each cell is provided with a  
25 water jacket to control the temperature of the contents of the cell.

DE-A-2742829 (Shiraishi Kogyo Kaisha) describes a plant for continuous production of precipitated

calcium carbonate in which droplets of calcium hydroxide suspension are sprayed countercurrently to a gas containing 10-40% by volume of carbon dioxide which flows upwards through a column, in a three stage process. The sizes of the suspension droplets in the three stages are, respectively, 0.2-1.0mm, 1.0-2.0mm and 1.5-2.0mm, and the degrees of carbonation achieved in each of the three stages are, respectively, 5-15%, 95-98% and 100%. This arrangement may be said to be a case of a reversed phase reaction, because droplets of liquid calcium hydroxide suspension are suspended in a gas phase.

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US-A-4888160 (Kosin et al.) describes a carbonation process for producing calcium carbonate from calcium hydroxide derived from limestone which provides improved utilisation of the carbon dioxide gas used in the carbonation process. A gas containing carbon dioxide is injected into a recirculating stream flowing in a recycle piping system which is in communication with a reaction vessel. The carbon dioxide-containing gas is injected at a turbulent point or area located in the recycle piping system, for example where the stream executes a 90° bend. Preferably at least one in-line static mixer is included in the recycle piping system, most preferably just downstream of the point of admission of the carbon dioxide-containing gas.

This is a recirculating, rather than a "straight through", system.

According to the present invention there is provided a method of continuously or semi-  
5 continuously producing a product comprising precipitated calcium carbonate in an aqueous medium which method comprises delivering an aqueous suspension of calcium hydroxide in sequence through a series of at least two static in-line mixers whilst  
10 carbon dioxide is introduced into the suspension at or before each of the mixers whereby carbon dioxide and the aqueous suspension are intimately mixed in each mixer to facilitate reaction of the carbon dioxide with calcium hydroxide dissolved in the  
15 aqueous medium, the calcium hydroxide in the suspension delivered to the series of static in-line mixers being progressively consumed and converted to calcium carbonate as the suspension passes through the series.

20 In the method according to the invention the series of in-line static mixers may comprise at least three such mixers, preferably from four to seven such mixers. Each of the static in-line mixers may comprise an outer casing and a plurality of internal  
25 static vanes or baffles which cause the treated aqueous suspension to undergo changes of direction, eg many rapid changes. Each of the static in-line mixers desirably permits carbon dioxide to be

uniformly distributed through the mixed suspension in the form of fine bubbles in the mixer.

The speed of the reaction in the method according to the invention depends, amongst other  
5 things, on the area of contact between the carbon dioxide-containing gas and the aqueous suspension of calcium hydroxide. This area of contact may be increased by ensuring that the carbon dioxide-containing gas travels through the suspension in the  
10 form of the smallest possible bubbles. It is therefore important that the gas enters the  
~~suspension in the form of small bubbles, that the~~  
bubbles are well dispersed throughout the suspension, and that the bubbles remain small substantially  
15 throughout their passage through the plant. The present invention allows these requirements to be met.

In the method according to the invention the aqueous suspension preferably enters the first of the  
20 series of mixers at a hydraulic pressure in the range 50kPa to 100kPa. The hydraulic pressure of the aqueous suspension is conveniently arranged to fall progressively as it passes through the series of static in-line mixers. Carbon dioxide delivered to  
25 be mixed with the suspension in the first in-line mixer in the series may be at a pressure in the range 50kPa to 150kPa. Carbon dioxide delivered to be mixed with the suspension in at least two subsequent

in-line mixers in the series may be at pressures reduced progressively from mixer-to-mixer. The carbon dioxide to be mixed with the suspension in each in-line static mixer may be delivered along a  
5 separate conduit for each mixture with the suspension. The carbon dioxide delivered along each conduit may be provided from a common carbon dioxide source. Each conduit may incorporate means for independently adjusting the pressure of the carbon  
10 dioxide delivered to be mixed with the aqueous suspension.

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~~In the method according to the invention the~~  
aqueous suspension in which the precipitated calcium carbonate is to be produced by reaction of calcium  
15 ions and carbonate ions from carbon dioxide may include non-consumable solids to be entrained by and/or bonded to the crystals of precipitated calcium carbonate produced in the aqueous medium. The non-consumable solids may comprise fibres, eg cellulose  
20 pulp fibres of the kind used in paper making, or present in a waste stream from a paper making operation. Where the fibres are present in a waste stream they may be present together with particulate material, eg a mixture of pigment or filler  
25 materials.

The non-consumable solids may have been obtained from an aqueous effluent of an industrial process, eg

a paper making, paper coating or paper de-inking process.

For example, where the aqueous suspension contains non-consumable solids which are fines from an industrial effluent the method may be carried out as described in Applicant's EP-A-604095A or EP-A-658606.

The aqueous medium may comprise mains water or it may alternatively comprise a dilute suspension of non-consumable solids, eg fibres and/or fine particulate waste material in which the fine particles are difficult to separate from the water by conventional means. Such dilute suspensions are produced, for example, as a white water waste stream of a process to produce sheets of paper in a paper mill. Such suspensions generally comprise fine solids known in the art as "fines" by which is meant those solids that are capable of passing through a round hole of diameter  $76\mu\text{m}$ . Generally, "fines" comprise fine cellulose and other fibrils and fine mineral particles, eg mineral particles of diameter of the order of  $2\mu\text{m}$  or smaller.

By the method of the present invention it is possible, in a continuous, rather than a batchwise, manner to produce a calcium carbonate containing product, optionally wherein non-consumable solid material, eg fibres and/or fines, is entrained and/or



bonded and thereby rendered useful in known applications as described later.

The calcium hydroxide employed in the aqueous medium in the method of the present invention may be prepared separately and added to the aqueous medium or alternatively may be prepared in situ in the aqueous medium for example by slaking calcium oxide. Where the aqueous medium comprises calcium hydroxide produced by slaking, the calcium hydroxide will be in the form of a suspension. Calcium ions will sparingly enter solution and will be continuously consumed and replaced as the reaction with carbon dioxide proceeds. Preferably, a suspension formed in this way contains between 0.5 mole and 3.0 moles, especially 1.0 to 2.0 moles, of the calcium hydroxide. For slaking, the temperature of the aqueous medium may be from 0°C to 80°C. The temperature will rise during the slaking process and if the aqueous medium is not at the appropriate temperature after slaking, it may be cooled before introduction of the carbon dioxide-containing gas.

Efficient dispersion and dissolution of the calcium hydroxide may be assisted by agitation, eg by stirring of the aqueous suspension, to provide uniform distribution of the particulate solid material comprising the hydroxide.

The aqueous medium in which the alkaline earth metal ions are contained and reacted with carbon

dioxide in the method according to the present invention may also contain one or more chemicals of a kind known for use in precipitate production, eg it may comprise a buffer solution to give the product  
5 so-called acid tolerance.

The carbon dioxide used in the method according to the invention may be substantially pure carbon dioxide eg as commercially supplied in a compressed gas cylinder or may be present in a mixture with  
10 other gases. The supplied carbon dioxide gas may alternatively be diluted with other inert gases, eg air, nitrogen, etc. The carbon dioxide may be  
present as a mixture of spent gases such as flue gases, eg obtained from a lime calcination plant in  
15 which quicklime is produced for conversion into slaked lime (for use in the process according to the first aspect).

The temperature of the aqueous medium when the carbon dioxide-containing gas is added thereto is  
20 preferably in the range of from 10°C to 80°C, especially 20°C to 60°C.

The calcium carbonate-containing precipitate product formed in the method according to the first aspect of the present invention may be further  
25 processed for example by dewatering and/or by subjecting the precipitate-containing suspension to comminution, eg by attrition grinding with an

attrition grinding medium, eg as described in Applicant's copending EP 96307320.0.

5 The precipitate product produced by the method according to the invention, whether formed of substantially pure precipitate calcium carbonate crystals or in the form of a precipitate-containing composite, may be employed in applications in which particulate precipitates of calcium carbonate formed are known to be useful.

10 Thus, the precipitate product may, for example, be employed as a particulate filler, pigment, ~~extender or property modifier in a known way in~~ compositions for manufacture of paper, paints, polymers, plastics, cements and ceramics, and  
15 articles made therefrom. The precipitate product may have properties selected for the particular application. The product may be treated by known chemical or physical processes, after production to render it suitable for the particular application.

20 A preferred form of the precipitate product for use as a fine pigment in a paper coating composition has a particle size distribution such that at least 70% by weight and desirably at least 90% by weight of the precipitate particles have an equivalent  
25 spherical diameter (as measured by sedimentation) of less than two micrometres. Desirably, at least 50% by weight (based on the dry weight of the product) have an equivalent spherical diameter of less than

0.5 micrometres. A preferred product particle size distribution for the precipitate product is one in which the particle size distribution is such that the percentage by weight of particles have an equivalent  
5 spherical diameter (measured by sedimentation) smaller than  $2\mu\text{m}$  is 50 per cent or more by weight.

The precipitate product will generally comprise either the rhombohedral or the scalenohedral variant of the calcite crystal form of calcium carbonate, or  
10 in the aragonite crystal form or a mixture of these forms. The crystal form in which the calcium  
~~carbonate is precipitated depends upon the reaction~~  
conditions.

As described in our EP 96307320.0 the conditions  
15 under which the method according to the first aspect is carried out may be chosen to give predominantly a selected crystal form of the precipitate product. The process conditions during the precipitation process required generally to achieve predominantly a  
20 preferred crystal form are well known to those skilled in the art. The crystal pcc form achieved in practice is, in any case, unlikely to be 100% of any selected form. It is quite usual for one crystal form even when predominant to be mixed with other  
25 forms. Such mixed forms will generally give suitable product properties.

The precipitate product in the form of an aqueous suspension preferably has a viscosity of not more than 500m Pa.s (as measured by a Brookfield Viscometer using a spindle speed of 100 rpm) and is  
5 preferably a pumpable and flowable slurry.

The precipitate product produced by the method according to the present invention may be mixed with other particulate materials known for use in the applications for the product, eg as mentioned above.

10 For example, where the precipitate product is to be employed as a pigment material for paper coating it may be mixed with one or more other pigment materials eg known materials selected from titanium dioxide, talc, calcium sulphate, kaolin clay,  
15 calcined kaolin and precipitated or ground calcium carbonate. A paper coating pigment mixture may beneficially include a mixture of the precipitate product and a kaolin clay. Such a pigment mixture may comprise from 5% to 99%, especially 20% to 70%,  
20 by weight of the precipitate product. For paper coating applications platey kaolin clay is especially preferred to form the pigment mixture with the precipitate product optionally together with other pigment ingredients by "platey" kaolin clay is meant  
25 a kaolin clay having an aspect ratio of at least 20:1, preferably at least 30:1.

A pigment mixture may be formed by mixing aqueous suspensions of each of the required pigments

to form an aqueous suspension incorporating the mixture of pigments. Such an aqueous suspension may be a dispersed aqueous suspension and the individual aqueous suspensions of pigments employed to form the mixture may each incorporate a dispersing agent. The dispersing agents employed to disperse the pigments in the individual aqueous suspensions mixed together, and the concentrations of such suspensions, may be the same or different.

10 A paper coating composition which comprises an aqueous suspension of a precipitate product produced by the method according to the present invention mixed together with a hydrophilic adhesive. The precipitate product employed in the composition may be mixed with one or more pigments as described above. The adhesive may form from 4% to 30% by weight based on the total dry weight of pigment or pigments present. The adhesive may be one of the known paper coating adhesives employed in the art, e.g. chosen from the group consisting of starches, proteinaceous adhesives such as casein and latices of, for example, styrene butadiene rubbers and acrylic polymers.

The paper coating composition produced using the precipitate product may also include one or more optional additives conventionally used in paper coating compositions, eg a thickener, e.g. in an amount of up to 2% by weight based upon the total dry weight of pigment or pigments present. The thickener

may comprise one or more substances known to be employed as thickeners in the prior art, e.g. sodium carboxymethyl cellulose or synthetic acrylic thickeners.

5           The said paper coating composition may be formed by mixing together an aqueous dispersed suspension containing the precipitate product optionally with one or more further aqueous dispersed suspensions containing other pigments, with the adhesive and any  
10 other optional constituents eg thickener, in a manner familiar to those skilled in the art.

~~..... The aqueous suspension containing the~~  
precipitate product formed in the method of the present invention may be treated so as to separate  
15 partially or fully the aqueous host medium from the precipitate product solids using one or more separation processes which may be known processes. For example, processes such as filtration, sedimentation, centrifugation or evaporation may be  
20 used. Filtration using a filter press is preferred. The separated aqueous medium, eg water, may, optionally with further purification or clarification by one or more chemical, biochemical or mechanical processes which may be known per se, may be recycled  
25 for reuse, eg in a paper mill, eg for use in diluting the paper making stock or for use as showers for washing machinery. The separated solids may be assessed for quality control by measurements taken on

samples and subsequently delivered to a storage tank and thereafter supplied as necessary for use in a user application, eg as described hereinbefore. The solids containing suspension may be re-diluted for  
5 use at the user plant.

It is not necessary for an aqueous suspension containing a precipitate product produced by the method of the present invention to be dewatered prior to supply for use in a user application, eg for use  
10 in a paper mill. The aqueous suspension or slurry may be delivered to a storage tank or directly to the user plant without substantial dewatering.

Where the precipitate product is to be used as a filler in a paper making composition the precipitate  
15 product may be supplied to the mill in one of various concentrations in water. The concentration may range from dilute suspension form to dry particulate solids. The precipitate product after formation in the method according to the present invention may or  
20 may not be treated as appropriate, eg by dewatering or not, so that it may be delivered to the user plant, eg paper making mill, in the required concentration.

The extent of dilution or concentration of the  
25 form in which the precipitate product is added to the user composition, eg paper making composition does not critically affect the properties of the resulting product, eg paper sheet. It may, however, for



economic and practical reasons be more suitable to supply the product in the form of a concentrated pumpable aqueous slurry. Where the product is supplied for use in a process at another location it  
5 may be preferable to dry the product prior to transport. Where the product has been concentrated or dried prior to delivery and subsequently re-dispersed in or diluted with clean water prior to re-use, the concentration and dilution steps do not  
10 materially affect the usefulness of the product.

In any event, where the precipitate product is to be used as a filler material in paper making, the precipitate product may, as will be clearly evident to those familiar with the paper making art, be  
15 blended in various proportions with conventional filler materials, eg precipitated or natural , eg ground, calcium carbonate, kaolin or other clay, metakaolin, talc, calcium sulphate etc., the ingredients and composition as well as the host  
20 fibres being selected according to the quality of paper required to be produced. In general, these materials are likely to be in slurry form when they are mixed.

The paper maker will normally select the  
25 concentration of the precipitate product (produced in accordance with the present invention) in aqueous suspension and the delivery rate of the suspension at the point of addition to the paper making

composition, eg finish. As noted above, this may require re-dilution of a suspension which has been delivered to the paper mill in concentrated form. Generally, the suspension added may contribute

5 precipitate product which forms optionally with other particulate fillers up to 30% by weight of the solids content of the paper making composition.

An embodiment of the present invention will now be described by way of example with reference to the  
10 accompanying drawings in which:

Figure 1 is a diagrammatic representation of the flow sheet of a plant for the continuous  
precipitation of calcium carbonate in an aqueous suspension containing a fine, non-consumable  
15 particulate material.

As shown in Figure 1, a suspension of fine solid material, eg derived from the waste water recovery system of a paper mill, the so-called "white water" is stored in a tank 1. The suspension has a total  
20 solids content which is generally in the range of from about 0.5% to about 8% by weight of solids on a dry weight basis, and the solids generally comprise a mixture of short cellulosic fibres such as would pass through a round hole of diameter  $76\mu\text{m}$  and of fine  
25 mineral filler particles substantially all of which have an equivalent spherical diameter smaller than  $1\mu\text{m}$ . The suspension is delivered by means of a pump 2 through a flow meter 3 into a conduit 4 at a

hydraulic pressure in the range of from 5 to 10 bar (50kPa to 100kPa). The pump is conveniently of the single-rotor screw pump type, for example of the Moyno or "MONO"™ type. This type of pump comprises a

5 metal rotor which rotates within and coaxially with an elastomeric stator, the rotor and stator being of such design that the fluid passing through the space between them is compelled to follow a substantially helical path. Pumps of this type are capable of

10 delivering liquids at pressures of up to about 20 bar or more. A suspension of calcium hydroxide, which may have a solids content in the range of from about 5% to about 40% by weight, is prepared in a tank 5 and is delivered by means of a pump 6, which may

15 conveniently be of the same type as pump 2, through a combined flow and density meter 7 and a throttle valve 8 to conduit 4, where the lime suspension mixes with the suspension of waste solid material. A portion of the calcium hydroxide delivered by pump 6

20 may be diverted through a throttle valve 9 back to tank 5. The proportion of calcium hydroxide suspension and waste solid material suspension in the mixture in conduit 4 may be determined by adjusting the settings of valves 8 and 9. The mixed suspension

25 is delivered under a pressure which is monitored by a pressure gauge 10 to an in-line static mixer 11 which effects thorough mixing of the calcium hydroxide with the waste solid material. The in-line static mixer

conveniently comprises a cylindrical outer casing and a large number of internal static vanes or baffles which cause the mixed suspension to undergo a large number of sudden changes of direction. In this way  
5 the turbulence of the suspension flowing in conduit 4 is increased and efficient mixing takes place.

The mixed suspension leaving in-line mixer 11 then passes through a series of six further in-line mixers 12, 13, 14, 15, 16 and 17, each of which is of  
10 similar general design to in-line mixer 11. Carbon dioxide gas under a pressure of 10 bar is delivered from supply means 18 through a conduit 19 to a manifold system, the pressure of the gas in conduit 19 being monitored by a pressure gauge 20. Carbon  
15 dioxide gas is metered to the upstream end of each of the in-line mixers 12 to 17 through throttle valves 21, 22, 23, 24, 25 and 26, respectively, the flow rate of gas to each of the in-line mixers 12 to 17 being monitored by flow meters 27, 28, 29, 30, 31 and  
20 32, respectively. The hydraulic pressure of the mixed suspension entering in-line mixers 13, 14, 15, 16 and 17 is monitored by pressure gauges 33, 34, 35, 36 and 37 respectively. The hydraulic pressure of the mixed suspension decreases as the suspension  
25 passes through each successive in-line mixer, and the calcium hydroxide present in the suspension is progressively converted to calcium carbonate through contact with the carbon dioxide gas, until the

suspension leaving the final in-line mixer 17 contains substantially no unconverted calcium hydroxide. The design of the in-line mixers is such that the carbon dioxide gas is uniformly dispersed  
5 throughout the mixed suspension in the form of extremely fine bubbles. This ensures that there is a very large area of contact between the gas and the suspension which enables the carbonation reaction to proceed rapidly, so that carbonation is substantially  
10 completed in the time taken for the suspension to pass through the series of in-line mixers.

The suspension containing precipitated calcium carbonate leaves the final in-line mixer 17 through a throttle valve 38 and the pH of this product  
15 suspension is monitored by a pH meter 39.

Examples of methods carried out using a plant as shown in Figure 1 are as follows.

#### **EXAMPLE 1**

20 A white water waste suspension from a paper mill contained 8% by weight of a mixture of solids which comprised both short cellulosic fibres and fine mineral filler particles. Dilution water was added to this suspension in sufficient quantity to reduce  
25 the solids concentration to 2.25% by weight and the diluted suspension was pumped by means of a Moyno pump at a rate of about  $27\text{kg}\cdot\text{min}^{-1}$  through a static in-line mixer to ensure homogeneity. A suspension

containing 20% by weight of calcium hydroxide was separately prepared, and this suspension was pumped by means of a Moyno pump at a rate of  $2.22 \text{ kg.min}^{-1}$  to combine with the waste suspension. The combined  
5 suspension passed at a rate of about  $29 \text{ kg.min}^{-1}$  through a static in-line mixer to ensure thorough mixing. The mixed suspension entered a series of static in-line mixers as described above with reference to Figure 1, except that the plant  
10 comprised five in-line mixers, rather than six. The mixed suspension entered the first in-line mixer under a hydraulic pressure of 6 bar.

Carbon dioxide gas under pressure was introduced into the mixed suspension as it entered each of the  
15 five in-line mixers under the conditions shown in Table 1 below:

TABLE 1

Mixer No	CO <sub>2</sub> Pressure (bar)	CO <sub>2</sub> Flow rate (l.min <sup>-1</sup> as measured at pressure shown in column 2)	Mass flow (kg.hr <sup>-1</sup> )
1	6	6	3.97
2	5	7.18	3.97
3	4	9	3.97
4	3	12	3.97
5	2	8	1.76
Total			17.63

The total rate of supply of carbon dioxide gas,  
5 namely about 18kg.hr<sup>-1</sup>, was slightly greater than the  
stoichiometric rate of about 16kg.hr<sup>-1</sup> which was  
calculated to carbonate completely the calcium  
hydroxide being supplied in the mixed suspension.

The precipitate product obtained from the final  
10 in-line mixer was a suspension in which the waste  
solids fines were entrained in and bonded to an  
approximately equal weight of precipitated calcium  
carbonate of good crystalline form. The product was  
found to have a good white colour and light  
15 scattering properties, and to be a very suitable

material for mixing with cellulosic fibres and other ingredients of a wet stock for feeding to the headbox of a paper making machine for paper making in the manner described earlier.

5

## EXAMPLE 2

Precipitated calcium carbonate was prepared by a continuous process using the apparatus described above with reference to Figure 1. A calcium  
10 hydroxide suspension containing 13.9% by dry weight of calcium hydroxide was pumped at a flow rate of 102 litre.hr<sup>-1</sup> together with 1980 litre.hr<sup>-1</sup> of water into the first of a series of six static in-line mixers under a hydraulic pressure of 7.3 bar. Carbon  
15 dioxide gas was introduced into the calcium hydroxide suspension at the upstream end of each in-line mixer and was dispersed throughout the suspension in each mixer in the form of very fine bubbles. In each  
20 mixer conversion of calcium hydroxide to calcium carbonate took place, so that the suspension leaving the final in-line mixer contained substantially no unconverted calcium hydroxide. The total rate of supply of carbon dioxide gas was 18.5 kg.hr<sup>-1</sup>. The  
25 flow rates of calcium hydroxide suspension and of carbon dioxide gas corresponded to rates of 210 moles of calcium hydroxide per hour and 420 moles of carbon dioxide per hour. The mixture of gas and suspension flowed evenly through each stage of the process



without the formation of plugs of gas. This indicated that the gas supplied at the upstream side of each in-line mixer was well absorbed by the calcium hydroxide in the suspension in that mixer.

5           The precipitated product was precipitated calcium carbonate having a predominantly rhombohedral crystal form. The particle size distribution of the calcium carbonate was such that 86% by weight consisted of particles having an  
10           equivalent spherical diameter smaller than  $5\mu\text{m}$  and 50% by weight consisted of particles having an equivalent spherical diameter smaller than  $2\mu\text{m}$ . The colour and brightness of the calcium carbonate was such that the reflectance to light of wavelength  
15           457nm was 92.8% and the reflectance to light of 570nm was 95.1%. The reflectance tests were carried out in accordance with International Standard No. ISO 2470.

### **EXAMPLE 3**

20           Calcium carbonate was precipitated in a suspension of a fine particulate waste material by a continuous process using the apparatus described above with reference to Figure 1. A suspension of the waste material was derived from the white water  
25           recovery circuit of a paper mill. It was pumped through a static in-line mixer together with a calcium hydroxide suspension containing 13.9% by dry weight of calcium hydroxide. The suspension of waste

material contained 2.45% by weight of dry fine particulate waste material, comprising a mixture of short cellulosic fibres and fine mineral filler material, ie "fines", and was pumped at a rate of about 2000kg.hr<sup>-1</sup>. The calcium hydroxide suspension was pumped at a rate of about 200kg.hr<sup>-1</sup>, so that the mixed suspension entered the first of a series of six static in-line mixers at a flow rate of about 2200kg.hr<sup>-1</sup> under a hydraulic pressure of 7.7 bar.

Carbon dioxide gas was introduced into the mixed suspension at the upstream end of each in-line mixer and was dispersed throughout the suspension in each mixer in the form of very fine bubbles. In each mixer conversion of calcium hydroxide to calcium carbonate took place, so that the suspension leaving the final in-line mixer contained substantially no unconverted calcium hydroxide. The total rate of supply of carbon dioxide gas was about 17kg.hr<sup>-1</sup>. The flow rates of calcium hydroxide suspension and of carbon dioxide gas corresponded to rates of 366 moles of calcium hydroxide per hour and 377 moles of carbon dioxide per hour. Again the mixture of gas and suspension flowed evenly through each stage of the process without the formation of plugs of gas.

The precipitate product was a suspension of composite particles of fines entrained by and bonded to crystals of precipitated calcium carbonate having a good white colour and crystal form. The composite

particles contained in the suspension were dewatered by filtration and the percentage reflectance to light of wavelengths 457nm and 570nm, respectively, were measured in accordance with ISO Standard No. 2470.

- 5 The filtration rate was also determined according to the method described in EP-A-0604095. The results are set forth in Table 2 below. The same tests were also performed on a dewatered sample of the original suspension of fine particulate waste material, and
- 10 the results are also given in Table 2 below for comparison.

**TABLE 2**

	Fine particulate waste material	Product embodying the invention
% reflectance to light of 457nm wavelength	76.4	83.7
% reflectance to light of 570nm wavelength	84.2	88.9
Filtration rate	0.063	0.6061

15

These results show that the precipitate product obtained by a method embodying the invention has a

desirable whiteness and brightness which renders it a  
very suitable material for mixing with cellulosic  
fibres and other ingredients of a wet stock for  
feeding to the headbox of a paper making machine for  
5 use as a filler in paper making in the manner  
described earlier. The filtration rate of a  
suspension containing the solid material has also  
been increased by a factor of about 10 which makes it  
much easier to separate from an aqueous medium in  
10 which it is suspended.

## CLAIMS

1. A method of continuously or semi-continuously producing a solid product comprising precipitated  
5 calcium carbonate in an aqueous medium which method comprises delivering an aqueous suspension of calcium hydroxide in sequence through a series of at least two static in-line mixers whilst carbon dioxide is introduced into the suspension at or before each of  
10 the mixers whereby carbon dioxide and the aqueous suspension are intimately mixed in each mixer to facilitate reaction of the carbon dioxide with calcium hydroxide dissolved in the aqueous medium, the calcium hydroxide in the suspension delivered to  
15 the series of static in-line mixers being progressively consumed and converted to calcium carbonate as the suspension passes through the series.
2. A method as claimed in claim 1 and wherein the  
20 series of in-line static mixers comprises at least three such mixers.
3. A method as claimed in claim 2 and wherein the series of in-line static mixers comprises from four to seven such mixers.
- 25 4. A method as claimed in claim 1, claim 2 or claim 3 and wherein each of the static in-line mixers comprises an outer casing and a plurality of internal

static vanes or baffles which cause the suspension to undergo changes of direction.

5. A method as claimed in any one of the preceding claims and wherein each of the static in-line mixers  
5 permits carbon dioxide to be uniformly distributed through the mixed suspension in the form of fine bubbles.

6. A method as claimed in any one of the preceding claims and wherein the aqueous suspension enters the  
10 first of the series of mixers at a hydraulic pressure in the range 50kPa to 100kPa.

7. A method as claimed in any one of the preceding claims and wherein the hydraulic pressure of the aqueous suspension progressively falls as it passes  
15 through the series of static in-line mixers.

8. A method as claimed in any one of the preceding claims and wherein carbon dioxide is delivered to be mixed with the suspension in the first in-line mixer in the series at a pressure in the range 50kPa to  
20 150kPa.

9. A method as claimed in claim 8 and wherein carbon dioxide is delivered to be mixed with the suspension in at least two subsequent in-line mixers in the series at pressures reduced progressively from  
25 mixer-to-mixer.

10. A method as claimed in any one of the preceding claims and wherein the carbon dioxide to be mixed with the suspension in each in-line static mixer is

delivered along a separate conduit for each mixture with the suspension.

11. A method as claimed in claim 10 and wherein the carbon dioxide delivered along each conduit is  
5 provided by a common source.

12. A method as claimed in claim 10 or claim 11 and wherein each conduit incorporates means for independently adjusting the pressure of the carbon dioxide delivered to be mixed with the aqueous  
10 suspension.

13. A method as claimed in any one of the preceding claims and wherein the aqueous suspension includes non-consumable solids to be entrained by and bonded to the precipitated calcium carbonate produced in the  
15 aqueous medium.

14. A method as claimed in claim 13 and wherein the non-consumable solids comprise fibres and/or particles.

15. A method as claimed in claim 13 and wherein the  
20 non-consumable solids comprise cellulose fibres and/or inorganic pigment particles.

16. A method as claimed in claim 14 or claim 15 and wherein the non-consumable solids comprise fines.

17. A method as claimed in claim 16 and wherein the  
25 fines have been obtained from an aqueous effluent of an industrial process.

18. A method as claimed in claim 17 and wherein the fines have been obtained from an aqueous effluent from a paper making or paper coating process.

19. A method as claimed in any one of the preceding  
5 claims and wherein the non-consumable solids constitute from 0.5% to 20% by weight of the aqueous suspension of the non-consumable solids in the aqueous medium.

20. A method as claimed in any one of claims 13 to  
10 19 and wherein the ratio by dry weight of the non-consumable solids to calcium hydroxide delivered to be mixed with carbon dioxide in the first in-line static mixer is in the range 1:10 to 10:1.

21. A method as claimed in claim 20 and wherein an  
15 aqueous suspension of the non-consumable solids and an aqueous suspension of the calcium hydroxide are mixed together in a static in-line mixer to produce the aqueous suspension to be delivered to the first in-line static mixer.

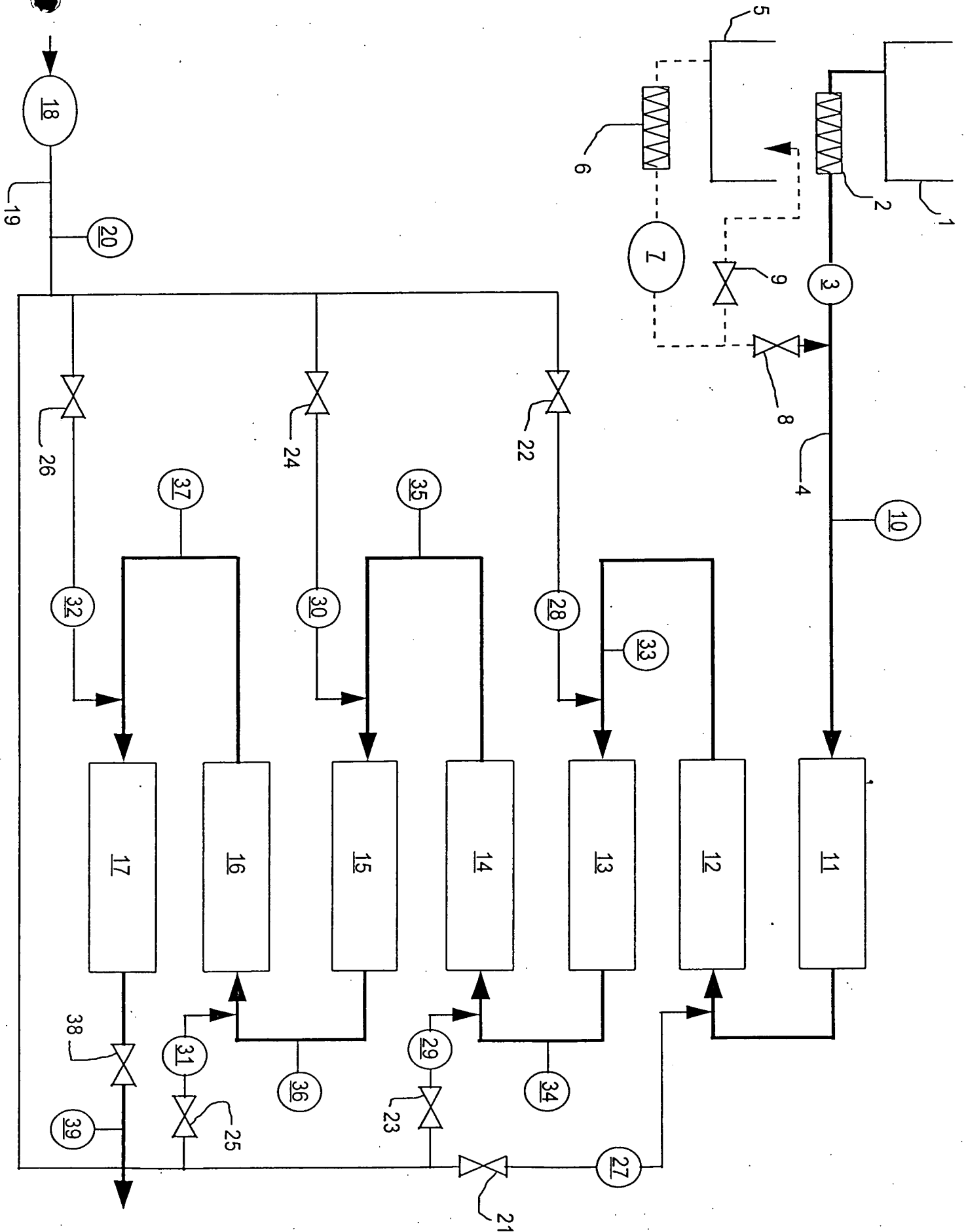
20 22. A method as claimed in claim 1 and substantially as hereinbefore described with reference to Figure 1 of the accompanying drawing.



**ABSTRACT**

A method of continuously or semi-continuously producing a solid product comprising precipitated calcium carbonate in an aqueous medium which method comprises delivering an aqueous suspension of calcium hydroxide in sequence through a series of at least two static in-line mixers whilst carbon dioxide is introduced into the suspension at or before each of the mixers whereby carbon dioxide and the aqueous suspension are intimately mixed in each mixer to facilitate reaction of the carbon dioxide with calcium hydroxide dissolved in the aqueous medium, the calcium hydroxide in the suspension delivered to the series of static in-line mixers being progressively consumed and converted to calcium carbonate as the suspension passes through the series.







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